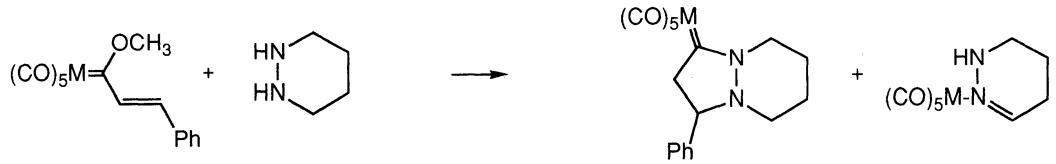
CHEMISTRY LETTERS, pp. 777-778, 1994.

Synthesis of (1,5-Diazabicyclo[4.3.0]nonan-2-ylidene)pentacarbonylchromium and -tungsten Using Reaction of 2-Unsaturated Carbene Complexes with 6-Membered Hydrazine

Masahiko IYODA,* Li ZHAO, and Haruo MATSUYAMA
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-03

The reaction of styryl carbene complexes of chromium and tungsten with 6-membered hydrazine proceeded smoothly to give the bicyclic carbene complexes, together with dehydropiperidazine complexes.

1,5-Diazabicyclo[4.3.0]nonan-2-one is known as a key intermediate of polyamine alkaloids dihydroperiphylline and celacinnine which show antitumor activity and depression of blood pressure.[1,2] Furthermore, 1,5-diazabicyclononanes possess an interesting framework as 5-aza-analogue of indolidine alkaloids. Recently we have found that the reaction of the unsaturated chromium and tungsten carbene complexes **1** and **5** with 6-membered hydrazine (piperidazine) **2** produces the aminocarbene complexes **3** and **6** having 1,5-diazabicyclo[4.3.0]nonane structure. Since aminocarbene complexes have been employed as a reactive amide which can be easily converted into the corresponding carbonyl derivatives, the complexes **3** and **6** might be a good precursor to interesting heterocyclic compounds (Scheme 1).[3]



1: M = Cr
5: M = W

2

Scheme 1.

3: M = Cr
6: M = W

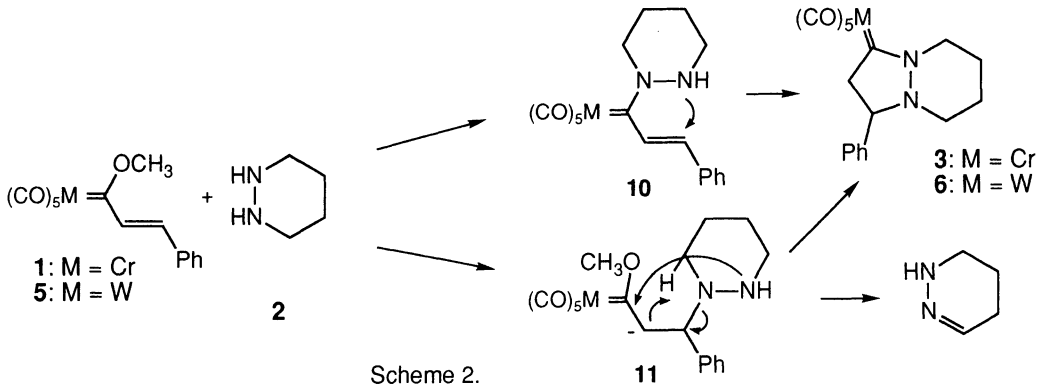
4: M = Cr
7: M = W

The reactions of **1** and **5** with **2** are summarized in Table 1. The reaction of the styryl carbene complex **1** (0.15 mmol) with freshly distilled **2** (0.3 mmol) in CH_2Cl_2 (2.5 cm^3) was carried out at room temperature for 4 h, and the products were separated by gel-permeation chromatography to give the bicyclic carbene complex **3**[4] in 59% yield, together with dehydropiperidazine-chromium carbonyl complex **4**[4] (24%). Although various solvents such as benzene, ether, and THF can be used in these reactions, the yields of the desired product **3** were 30-35%, and considerable amounts of the by-product **4** were formed. In a similar manner, from the reaction of the unsaturated tungusten complex **5** with **2** in CH_2Cl_2 at room temperature for 4.5 h, the bicyclic carbene complex **6**[4] was obtained in 41% yield, together with **7**[4] (15%), whereas the reaction of **5** with **2** in THF gave **6** in 32% yield with a small amount of **7**. The carbene complexes **3** and **6** are rather stable and can be stored in a refrigerator. Oxidation of **3** and **6** with iodoso-benzene in CH_2Cl_2 afforded 4-phenyl-1,5-diazabicyclo[4.3.0]nonan-2-one in 70 and 41% yields, respectively.

Table 1. Reactions of styryl carbene complexes of chromium and tungustene **1** and **5** with **2**.

Compound	Solvent	Time/ h	Products/ %	
1	CH_2Cl_2	4	**3** (59)	**4** (24)
1	benzene	2.5	**3** (32)	**4** (24)
1	ether	0.5	**3** (30)	**4** (27)
1	THF	0.5	**3** (35)	**4** (27)
5	CH_2Cl_2	4.5	**6** (41)	**7** (15)
5	THF	0.5	**6** (32)	**7** (4)

The formation of the bicyclic carbene complexes **3** and **6** can be explained by two pathways. In one mechanism, the first reaction is the pathway to the aminocarbene complex **10** which cyclizes to give **3** and **6**. In another mechanism, the first step is the conjugate addition of **2** to give the corresponding alkoxycarbene complex **11** which leads to **3** and **6** and/ or **4** and **7** (Scheme 2).[5]



Scheme 2.

References
1) H. H. Wasserman, R. P. Robinson, and H. Matsuyama, *Tetrahedron Lett.*, **1980**, 3493.
2) H. H. Wasserman and H. Matsuyama, *J. Am. Chem. Soc.*, **103**, 461 (1981).
3) B. A. Anderson, W. D. Wulff, and A. Rahm, *J. Am. Chem. Soc.*, **115**, 4602 (1993).
4) The structure of **3**, **4**, **6** and **7** were fully characterized by the spectroscopic analysis. **3**: yellow oil, MS (EI) 392 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H), 4.85(d, J=11.7 Hz, 1H), 3.91-3.75 (m, 3H), 3.22 (d, J=11.7 Hz, 1H), 3.06 (m, 1H), 2.52 (m, 1H), 2.09-1.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.1 (carbene carbon), 222.7 (CO), 217.9 (4CO), 139.6, 128.9, 128.1, 126.9, 68.5, 61.4, 56.8, 53.5, 24.5, 23.3. **4**: yellow crystal, mp 53 °C (decomp.); MS (EI) 276 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 6.98 (br s, 1H), 4.96 (br s, 1H), 3.09 (br s, 2H), 2.25 (br s, 2H), 1.86 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.3 (CO), 214.2 (4CO), 152.2, 44.2, 25.4, 18.0. **6**: yellow oil, MS (EI) 526, 524, 522 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 5H), 4.82 (d, J=12.2 Hz, 1H), 3.91-3.81 (m, 2H), 3.67 (br t, J=13.2 Hz, 1H), 3.24 (br d, J=12.2 Hz, 1H), 3.06-2.97 (m, 1H), 2.58-2.51 (m, 1H), 2.08-1.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2 (carbene carbon), 202.8 (CO), 198.1 (4CO), 139.4, 128.9, 128.1, 126.9, 69.4, 62.9, 56.5, 54.9, 24.4, 23.2; IR (neat) 2061 (νCO), 1887 (νCO) cm^{-1}. **7**: yellow crystal, mp 84 °C (decomp.); MS (EI) 410, 408, 406 (M^+); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (br s, 1H), 5.12 (br s, 1H), 3.15 (br s, 2H), 2.31 (br s, 2H), 1.93 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9 (CO), 198.5 (4CO), 154.1, 44.3, 25.5, 17.
5) The reaction of $(CO)_5CrC(OCH_3)CH_3$ with **2** formed the aminocarbene complex $(CO)_5Cr(NC_4H_8NH)CH_3$, whereas the reaction of $Cr(CO)_6$ with **2** afforded the piperidazine-chromium complex $[(CO)_5Cr(NHC_4H_8NH)]$.

(Received January 24, 1994)